EFFECT OF THERMAL CYCLING ON STRESS IN METALLIC FILMS ON CERAMIC SUBSTRATES

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INTRODUCTION

The hydrogen maser is the most stable frequency standard currently available for averaging intervals of hours to weeks. A major contributor to maser frequency variations is the maser's microwave resonant cavity: by means of the cavity pulling effect, a change in the cavity's resonance frequency produces a proportional change in the maser's output frequency. To minimize variations in the cavity's dimensions, and thus in its resonance frequency, maser cavities are often constructed of a low-expansivity glass-ceramic material coated on its inner surface with a conducitive metallic film. We have previously shown[1] that silver films like those used in SAO maser cavities develop tensile stress when cooled to room temperature after being fired onto the cavity, and that the stress in such films relaxes with time at a rate proportional to the level of stress. Stress relaxation in maser cavity coatings can alter the shape, and hence the resonance frequency, of the cavity, resulting in a slow variation in the maser's output frequency.

In the present work we have investigated the possibility of reducing or reversing the initial tensile stress by precooling the coated cavity material. We hypothesize that cooling the material well below its normal working temperature and then warming it to its normal temperature would result in a lower tensile stress or even a compressive stress. Under such a condition stress relaxation, and thus any consequent frequency drifts, might be reduced or reversed.

EXPERIMENT DESCRIPTION

MATERIAL SAMPLES AND MEASUREMENT SYSTEM

Measurements were made on eight samples of silver-coated low-expansion materials; these were among the samples whose shapes had been measured over a span of approximately eight years in the previous work on stress relaxation[1]. The samples are approximately 3.94 inches long, 0.75 inches wide, and 0.25 inches thick; they are optically polished on one face and coated with silver on the opposite face. Details of the sample preparation are given in reference 3. The substrate materials and film thicknesses for the samples are shown in Table 1.[2]

The silver film stress was determined from measurements of the sample shapes. The bending of the samples relative to a reference optical flat was measured by an optical interferometer equipped with a phase measuring adaptor. The adaptor digitized the interferograms formed by the interferometer and transferred the data to a computer, which analyzed the sample shapes using curve-fitting software.

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Table 1 -- Sample Materials

Plate	Material	Coating Thickness (.001 inch)
4	Zerodur	6.25
6	Cervit	uncoated
7	Cervit	4.88
9	Cervit	4.20
11	Cervit	1.00
24	ULE	4.37
28	ULE	1.95
30	ULE	1.05

EXPERIMENTAL PROTOCOL

The measurements were carried out during the period 25-28 June 1990. To obtain a knowledge of the samples' shapes before chilling, we first measured the sample shapes near room temperature. During measurement the samples were housed in an insulated, temperature-controlled chamber. The chamber's air temperature was measured using a calibrated thermistor driven by a constant current supply. To determine the incremental rate of change of coating stress with temperature and thus to be able to correct for small temperature variations, we measured the samples at approximately 25°C and 33°C, allowing several hours for the samples to equilibrate at each temperature.

Following the baseline curvature measurements, we removed the samples from the measurement chamber. A soft black deposit that had been deposited by vapor emitted by the chamber's insulation was removed by gentle wiping with acetone. Also, a deposit of adhesive on sample 11 from a strip of double sided tape was removed by rubbing with Alconox cleaner dissolved in water. Care was taken not to distort the samples during cleaning. We then immersed plates 4, 7, 11, 24, and 28 in liquid nitrogen for approximately 1.5 hours, after which we returned all of the plates to the sample chamber and measured their shapes several times during the following three days, at 25°C and 33°C.

DATA ANALYSIS

The shape analysis program determines the shape of the samples from the digitized interferogram. The fringe pattern produced by the interferometer is a function of the optical path difference (OPD) between the sample and a reference optical flat, and thus contains the sample shape. The program expresses the sample's shape by fitting a set of orthogonal Zernike polynomials to the OPD pattern. The coefficients of the first two polynomials, C_1 and C_2, express the average tilt of the sample relative to the flat, while the third Zernike coefficient, C_3, is proportional to the sample's curvature, referred to in optics terminology as "focus".

The sample curvature K is given by

$$K = \frac{4\,C_3}{r_0^2} \qquad (1)$$

where r_0 is the radius of the circle that circumscribes the (rectangular) interferogram.

The stress σ in the silver film parallel to the surface of the sample is proportional to the sample curvature[1]:

$$\sigma = K \frac{E}{6(1-\nu)} \frac{t_s^2}{t_f} \qquad (2)$$

where E and ν are the Young's modulus and Poisson's ratio, respectively, of the substrate material, t_s is the thickness of the substrate, and t_f is the film thickness. Because the samples were not completely flat in their unstressed state prior to being silver coated, the value of K in Eq. 2 must be the difference between sample's measured curvature and its initial (precoating) curvature.

The film stresses calculated from the fitted Zernike coefficients are plotted against elapsed time in Fig. 1.

DISCUSSION OF RESULTS

ACCURACY OF ZERNIKE POLYNOMIAL FIT

In calculating the sample curvature and film stress from the third Zernike coefficient, C_3, we assume that a three-parameter Zernike fit well represents the shape of the sample. A measure of that assumption is given by comparing $C_3(3)$ and $C_3(8)$, the values of C_3 resulting from a three-parameter Zernike fit and an 8-parameter fit, respectively. For samples 4, 6, 7, 9, 11, and 28 these coefficients generally agree to within about 10 to 15 percent, indicating that the three-parameter fit represents the sample shape well. For samples 24 and 30, however, $C_3(3)$ and $C_3(8)$ differ by up to roughly 50% for some measurements. Examination of the sample profiles given by the curve-fitting program show that sample 24 has a significant amount of asymmetrical curvature, which is represented by Zernike functions higher than order 3. Sample 30 has very little curvature, as indicated by small values of C_3, and its shape is only partially represented by the third Zernike polynomial.

EFFECT OF CHILLING: LIMITING FILM STRESS

Figure 1 reveals many similarities in the behavior of the coatings. The baseline measurements before chilling the samples show that all of the coatings had surface stresses of between roughly -1×10^7 and -2×10^7 N/m^2 at a temperature of 25°C. (The interferogram radius for plate 7's baseline measurement at 25°C was inadvertently not obtained from the program, so the coating stress could not be calculated for that measurement.) Negative stress values represent tensile film stresses. All of the coated samples were under tensile stress before being chilled.

After the plates 4, 7, 11, 24, and 28 were immersed in liquid nitrogen and rewarmed to room temperature, their film stresses were between $+2.0 \times 10^7$ and $+2.5 \times 10^7$ N/m^2. (Plate 30 was not chilled because its baseline curvature was not well defined, and plate 9 was preserved as an undisturbed sample.) The consistency of the post-chilling stress confirms that the film stress is limited by the yield strength of the silver material. The yield strength of bulk silver[3] ranges between 1.0×10^7 N/m^2 and 5.4×10^7 N/m^2. Thus the maximum stress resulting from chilling and warming the samples is consistent with the yield strength of silver.

INCREMENTAL STRESS CHANGE WITH TEMPERATURE

The existence of a limiting value for the film stress is also indicated by measurements of the incremental change in stress with temperature. When the samples were raised monotonically from 25°C to 33°C after chilling, the film stress increased by an amount substantially smaller than the corresponding increase observed in the baseline (prechilling) measurements. When the temperature was then returned to 25°C, the stresses decreased by amounts comparable to, although smaller than, the baseline changes. The rates of change of stress with temperature are given in Table 2.

Table 2 -- Rate of Change of Film Stress with Temperature

	$d\sigma/dT$ (10^5 Nm^{-2} $°C^{-1}$)		
Plate	25°C→33°C Prechilling	25°C→33°C Postchilling	33°C→25°C Postchilling
4	8.2	2.0	7.0
7	---	0.096	7.9
11	6.0	0.41	4.9
24	6.5	1.3	4.9
28	7.8	3.1	6.2
Not chilled:			
9	7.4	6.4	6.3
30	6.4		6.7

The measurements $d\sigma/dT$, together with the existence of a limiting film stress, have implications for maser performance. A coated maser cavity brought monotonically to room temperature from its firing temperature will have a tensile coating stress limited to approximately $2x10^7$ Nm^{-2}. Because the incremental rate of change of film stress with temperature is roughly $+6x10^5$ Nm^{-2} $°C^{-1}$, raising the cavity's temperature by approximately 30°C ($\approx 2x10^7/6x10^5$) is expected to reduce the film stress roughly to zero. Lowering the stress in this way reduces any cavity deformation due to stress relaxation, and thus reduces or eliminates the contribution of film stress to long-term frequency drift. SAO masers operate with a cavity temperature of 50°C, 30°C above room temperature, which satisfies the criterion for stress reduction.

STRESS CHANGE WITH TIME

The data of Fig. 1 indicate that the stress in the post-chilled films decreased over the period of observation. This agrees with earlier measurements[1] that showed that the stress in the coatings relaxed at a rate proportional to the internal stress. The stress in plate 9, which had not been chilled, decreased slightly in magnitude (became less negative). The data for plate 30 do not indicate a temporal stress change; this may be due to the small initial stress, or to the marginal representation of sample curvature by C_3. In order to obtain quantitatively significant values for the stress change with time, measurements over considerably longer periods would be needed.

CONCLUSIONS

The measurements confirm the hypothesis that prechilling metal-coated substrates can decrease or reverse the internal film stress, and that the stress is limited by the yield strength of the film material. Thus improper temperature treatment of hydrogen maser cavities can result in high coating stress and consequent frequency drift due to long-term stress relaxation. However, as discussed above, proper temperature cycling prior to operation can reliably reduce the surface stress in hydrogen maser cavities to a level where stress relaxation is not an important factor in maser frequency stability.

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REFERENCES

[1] E. M. Mattison and R.F.C. Vessot, "Time and temperature stability of silver-coated ceramics for hydrogen maser resonant cavities," *Proc. 20th Annual Precise Time and Time Interval (PTTI) Applications and Planning Meeting*, p. 313 (1988).

[2] Zerodur is a trademark of Schott Glasswork, Inc.; Cervit is a trademark of Owens-Illinois, Inc.; and ULE is a trademark of Corning, Inc.

[3] J.L. Everhart, W.E. Lindlief, J. Kanegis, P.G. Weissler, and F. Siegel, "Mechanical properties of metals and alloys", NBS Circular C447. U.S. Government Printing Office, 1943.

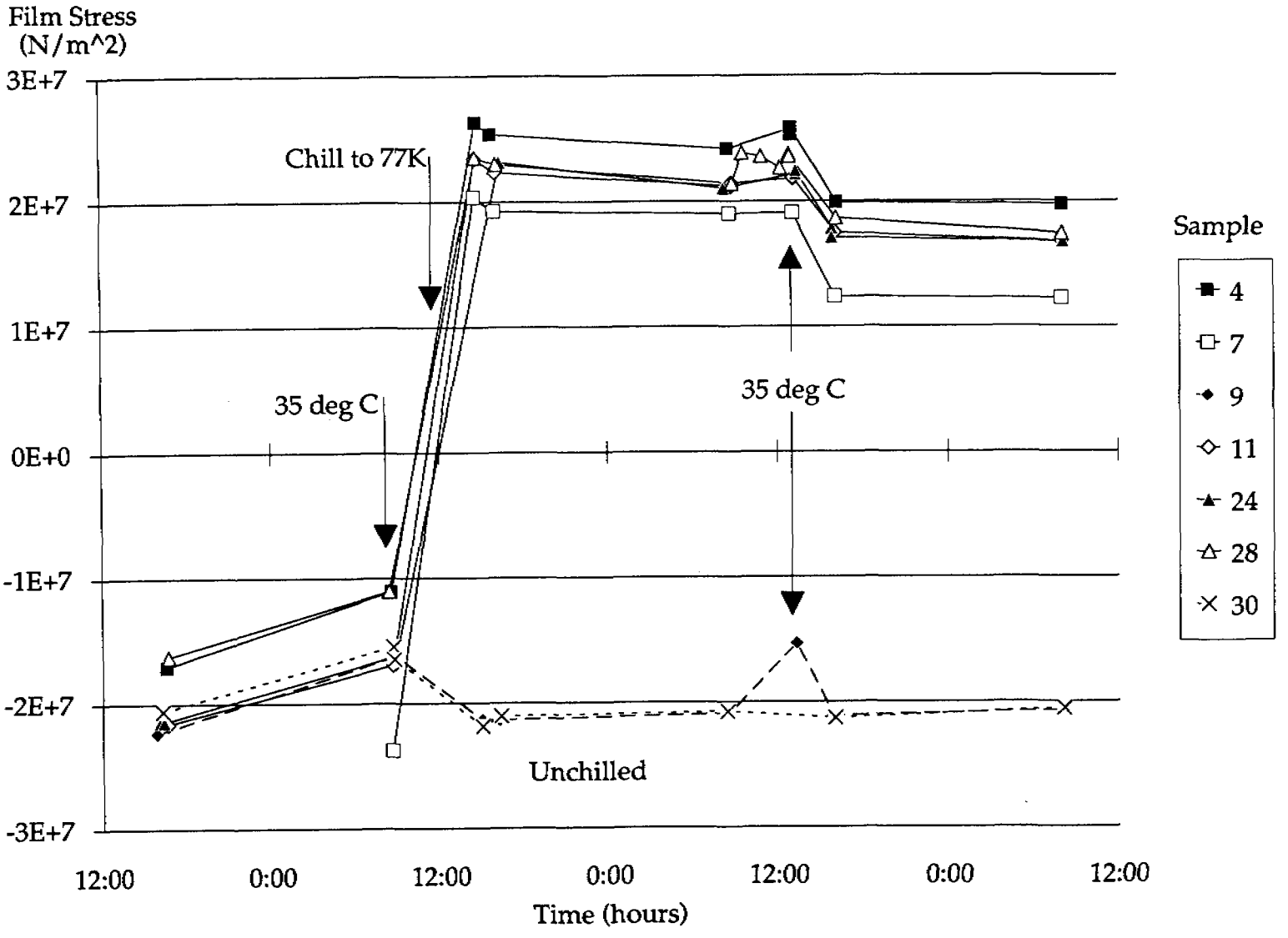

Fig. 1. Film stress as functions of time and temperature cycling
(Measurements at 25°C except as noted)